

Effective dynamics for a kinetic Monte-Carlo model with slow and fast time scales

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December 11, 2013

Abstract

We consider several multiscale-in-time kinetic Monte Carlo models, in which some variables evolve on a fast time scale, while the others evolve on a slow time scale. In the first two models we consider, a particle evolves in a one-dimensional potential energy landscape which has some small and some large barriers, the latter dividing the state space into metastable regions. In the limit of infinitely large barriers, we identify the effective dynamics between these macro-states, and prove the convergence of the process towards a kinetic Monte Carlo model. We next consider a third model, which consists of a system of two particles. The state of each particle evolves on a fast time-scale while conserving their respective energy. In addition, the particles can exchange energy on a slow time scale. Considering the energy of the first particle, we identify its effective dynamics in the limit of asymptotically small ratio between the characteristic times of the fast and the slow dynamics. For all models, our results are illustrated by representative numerical simulations.

1 Introduction

Langevin dynamics is commonly used in computational statistical physics to model the evolution of atomistic systems at finite temperature. The state of the system evolves according to a stochastic differential equation, and is thus modelled as a real vector valued Markov process. Generically, the state space of such atomistic systems can be decomposed into several metastable regions, separated by high energy barriers. It is therefore natural to introduce kinetic Monte-Carlo models as a simplification of the continuous-in-space reference model, where the state space is coarse-grained into discrete states that each corresponds to a metastable region of the continuous model. We refer e.g. to [11] for a formalization of this idea. The resulting dynamics is a time continuous Markov chain, also called jump process.

In this work, we consider such a jump process, with the particularity that two different time scales are present in the system. On a typical trajectory, many jumps of the fast degrees of freedom occur before a significant evolution of the slowly varying variables is observed. Therefore, a direct discretization is numerically very costly (this problem is known as the small barrier problem). The aim of this work is to find an effective dynamics for the slow variables (which turns out to be again a kinetic Monte Carlo model) while filtering out the fast variables. This effective dynamics is derived in the regime of large time scale separation between the slow and the fast variables.

We will successively perform this derivation for three different models.

First, in Section 2, we consider a particle subjected to a potential energy presenting two macro-states separated by a high energy barrier. Inside each macro-state, there are finitely many micro-states separated by relatively low energy barriers (see Fig. 1). The ratio between the low energy barriers and the large energy barriers is characterized by a parameter ϵ that we will take asymptotically small. This ratio encodes the difference of time scales between the dynamics within a macro-state (only low energy barriers have to be overcome, and the dynamics is therefore fast), and the global dynamics (for which large energy barriers have to be overcome, making this dynamics slow). See Section 2.1 for a complete description of the model.

We are interested in the long time behavior of functions of the slow variables. We consider in this article the simplest case of such function, that is, the macro-state in which the particle is located. At the price of additional technicalities, our approach carries over to more general functions of the slow variables.

Under an irreducibility assumption on the dynamics within the macro-states, we prove that, in the limit of asymptotically large time scale separation (namely when ϵ goes to zero), the dynamics of the slow variable converges to a jump process over the two macro-states. The transition rates of this limiting process are, in some sense, the weighted averages of the transition rates of the reference model. We underline that our convergence is a convergence on the *path* of the system, and not only on the state of the system at any given time. Our main result, Theorem 2.3, is presented in Section 2.1 and proved in Section 2.2.

In Section 2.3, we present detailed numerical results illustrating our theoretical conclusions. In particular, we monitor the probability distribution of the first waiting time in a macro-state, and check that this distribution indeed converges to the asymptotic distribution.

In Section 3, we turn to our second model, which is a generalization of the model considered in Section 2 where the potential energy presents *infinitely many* macro-states instead of two. To simplify the problem, we assume that the internal dynamics within each macro-state are identical (see Section 3.1 for a detailed presentation of the model). In this case, the effective dynamics is a time continuous random walk with Poissonian waiting times, as stated in our main result of that Section, Theorem 3.1. We provide some representative numerical results in Section 3.2.

We finally turn in Section 4 to our third model, which is different in spirit from the models studied in Sections 2 and 3. One interest of this last section is to show that the arguments employed to analyze the first two models can be used to study a model different in nature. The system at hand in Section 4 contains two particles, each one being described by k spin-like variables. The system evolves either due to the internal evolution of each particle (which occurs on a fast time-scale), or due to the interaction between the two particles (which occurs on a slow time-scale). In the first case, the energy of each particle is preserved while in the second, there is an exchange of energy between the two particles. Note that the total energy of the system is preserved in both cases. Our quantity of interest is the energy of the first particle, which is indeed a slow observable (see Section 4.1 for a complete description of the model). We show that the dynamics of the first particle energy converges to a jump process on the (finite) set of admissible energies, this set being determined by the initial energy (see Section 4.2, Theorem 4.1, for our main result). We collect in Section 4.3 some numerical illustrations.

The difficulty of the question we address stems from the fact that the slow observable is not a Markov process: this is a closure problem. A typical tool in this context is the Mori-Zwanzig projection formalism, which is described in details in [6]. This leads to approximating the slow observable by a process which has some memory in time. In our work, we assume that a time-scale separation is present in the system. Memory effects may then be neglected, and the slow observables be approximated by a Markov process. As often the case in such settings, an essential ingredient of our proof is an averaging principle (see [15] for a comprehensive review of that principle in various contexts). We refer to [5, 14, 17, 18] for related works in the framework of discrete time Markov chains in a discrete state space.

As pointed out above, kinetic Monte Carlo models are somewhat obtained as a coarse-grained approximation of real valued Markov processes, such as the Langevin equation (or its overdamped limit). In that framework, the construction and the analysis of effective dynamics has been undertaken in several works, see e.g. [12, 13] and the comprehensive bibliography contained therein.

Throughout this paper, we use several well-known results that we recall in Appendix A below.

2 A particle in a potential energy landscape with two macro-states

In this section we study the dynamics of a particle in a potential energy with two macro-states (see Fig. 1). The state of the particle is represented by a macroscopic variable (the index of the macro-state), which can take here only two values, and a microscopic variable (the index of the micro-state within the macro-state). We are concerned with the long time behaviour of the macroscopic variable. In Section 2.1, we present the model and state our convergence result (Theorem 2.3), the proof of which is given in Section 2.2. Numerical results illustrating our theoretical conclusions are gathered in Section 2.3.

2.1 Presentation of the model and main result

We now formalize the model described above. We introduce a parameter ϵ which represents the ratio between the characteristic time of the internal dynamic inside a given macro-state (fast time scale) and the characteristic time of evolution of the macro-state, namely the characteristic time the

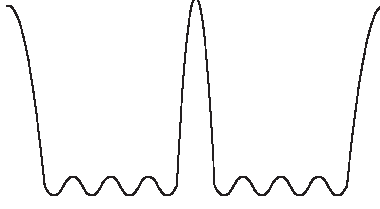


Figure 1: Example of a potential energy with two macro-states of energy wells.

system spends in a given macro-state before going to the other one. For simplicity, we assume that both macro-states contain the same number of micro-states. The macro-states are labelled by 0 and 1, whereas the micro-states are labelled as $1, 2, \dots, m$. We set $M = \{1, 2, \dots, m\}$.

The state of the particle is modelled by a time continuous Markov chain $\overline{Y}_t^\epsilon = (\overline{X}_t^\epsilon, \overline{Z}_t^\epsilon)$, which takes its values in the space $E = M \times \{0, 1\}$. The first coordinate of \overline{Y}_t^ϵ represents the micro-state of the particle inside a given macro-state, and thus takes its value in M . The second coordinate determines in which macro-state the particle is located at time t : $\overline{Z}_t^\epsilon = 0$ or 1 .

We denote by \overline{Q}^ϵ the transition matrix of the process \overline{Y}_t^ϵ . Let Q_0 and Q_1 be two $m \times m$ matrices that determine the internal dynamic within each macro-state and let $C_{0,1}$ and $C_{1,0}$ be two $m \times m$ matrices that determine the coupling between micro-states that belong to different macro-states. The transition rates of \overline{Y}_t^ϵ are given by

$$\begin{aligned} \overline{Q}^\epsilon((x, z), (x', z)) &= Q_z(x, x'), \quad z = 0 \text{ or } 1, x \neq x', \\ \overline{Q}^\epsilon((x, z), (x', z')) &= \epsilon C_{z,1-z}(x, x') \quad \text{for } z \neq z'. \end{aligned}$$

Thus, \overline{Q}^ϵ is of the form

$$\overline{Q}^\epsilon = \begin{pmatrix} Q_0 & \epsilon C_{0,1} \\ \epsilon C_{1,0} & Q_1 \end{pmatrix}.$$

Remark 2.1. *As always for Markov jump processes, the diagonal entries of the transition matrix are irrelevant. Our convention is to take them equal to zero.*

The process \overline{Y}_t^ϵ is a jump process. It means that, when it is in a state (x, z) , then

- it stays there for a time S , which is a random variable distributed according to an exponential distribution of parameter

$$\bar{q}^\epsilon(x, z) := \sum_{\substack{(x', z') \in E \\ (x', z') \neq (x, z)}} \bar{Q}^\epsilon((x, z), (x', z')),$$

that is $\mathbb{P}(S \leq t) = 1 - \exp(-\bar{q}^\epsilon(x, z)t)$.

- At this time S , it jumps to another state. The probability that it jumps to the state $(x', z') \neq (x, z)$ is given by

$$\frac{\bar{Q}^\epsilon((x, z), (x', z'))}{\bar{q}^\epsilon(x, z)}.$$

Note that the paths of a jump process are by convention right continuous, with left limits (they are thus càd-làg functions).

We are interested in the behaviour of a macroscopic observable, that is a function of the slow variable \bar{Z}_t^ϵ . The dynamic inside a given macro-state, i.e. when the variable z does not change, has a characteristic time of the order of $O(1)$ (i.e. independent of ϵ), whereas the characteristic time for the particle to go from one macro-state to the other is of the order of $O(\epsilon^{-1})$. We therefore consider henceforth the rescaled-in-time process $\left(\bar{Z}_{t/\epsilon}^\epsilon\right)_t$. We introduce the process $Y_t^\epsilon := \bar{Y}_{t/\epsilon}^\epsilon$, which is a jump process of intensity matrix Q^ϵ given by

$$Q^\epsilon = \begin{pmatrix} \epsilon^{-1}Q_0 & C_{0,1} \\ C_{1,0} & \epsilon^{-1}Q_1 \end{pmatrix}. \quad (1)$$

We assume that

$$\text{the matrices } Q_0 \text{ and } Q_1 \text{ are irreducible,} \quad (2)$$

therefore admitting unique invariant measures denoted by π_0 and π_1 , respectively.

Remark 2.2. Due to our convention on the transition matrix (see Remark 2.1), the invariant measure π of a transition matrix $Q = \{q_{i,j}\}_{1 \leq i,j \leq m}$ satisfies $\pi^T Q = \pi^T \Delta$, where Δ is a diagonal matrix with $\Delta_i = \sum_{j=1}^m q_{i,j}$.

Definitions and notations We denote by $D_{\mathbb{R}}[0, \infty)$ the set of càd-làg functions defined on $[0, \infty)$ and valued in \mathbb{R} , and by $C_{\mathbb{R}}[0, \infty)$ the set of continuous functions defined on $[0, \infty)$ and valued in \mathbb{R} . Endowed with the Skorohod metric (see e.g. [4, p. 116–118]), $D_{\mathbb{R}}[0, \infty)$ is a complete separable space.

A family of probability measures \mathcal{P}_n on $D_{\mathbb{R}}[0, \infty)$ is said to *weakly* converge to a probability measure \mathcal{P} on $D_{\mathbb{R}}[0, \infty)$ if, for any bounded continuous function Φ on $D_{\mathbb{R}}[0, \infty)$,

$$\lim_{n \rightarrow \infty} \int \Phi d\mathcal{P}_n = \int \Phi d\mathcal{P}.$$

A family of random variables X_n valued in $D_{\mathbb{R}}[0, \infty)$ is said to converge *in distribution* to $X \in D_{\mathbb{R}}[0, \infty)$ if the distribution of X_n weakly converges to the distribution of X . Otherwise stated, the family X_n converges in distribution to X if, for any bounded continuous function Φ on $D_{\mathbb{R}}[0, \infty)$, we have

$$\lim_{n \rightarrow \infty} \mathbb{E}[\Phi(X_n)] = \mathbb{E}[\Phi(X)].$$

Throughout this article, we use the symbol \Rightarrow for the convergence in distribution of càd-làg stochastic processes or the weak convergence of their corresponding distributions.

Main result We are now in position to present the main result of this section. For $z \in \{0, 1\}$, we define

$$\overline{C}_{z,1-z}(x) = \sum_{x' \in M} C_{z,1-z}(x, x')$$

and

$$\lambda_z = \sum_{x \in M} \overline{C}_{z,1-z}(x) \pi_z(x) = \sum_{x \in M} \pi_z(x) \sum_{x' \in M} C_{z,1-z}(x, x'). \quad (3)$$

Theorem 2.3. *Let $Y_t^\epsilon = (X_t^\epsilon, Z_t^\epsilon)$ be the jump process of intensity matrix (1) and starting from an initial condition $Y_0 = (X_0, Z_0)$ independent of ϵ . We make the assumption (2). We denote by \mathcal{P}^ϵ the distribution of the process (Z_t^ϵ) and by \mathcal{P} the distribution of the jump process of initial condition Z_0 and of intensity matrix*

$$\begin{pmatrix} 0 & \lambda_0 \\ \lambda_1 & 0 \end{pmatrix}, \quad (4)$$

where λ_0 and λ_1 are defined by (3). Then, we have $\mathcal{P}^\epsilon \Rightarrow \mathcal{P}$ as ϵ goes to 0.

Note that, in (4), we have used the convention detailed in Remark 2.1.

The above result confirms the intuition according to which, when ϵ goes to zero, the internal dynamic within each macro-state is speeded up, thus attaining a local equilibrium where configurations are distributed according to the invariant measures π_0 and π_1 within the macro-states. In the limit when ϵ goes to 0, the transition from one macro state z to the other one, $1-z$, occurs with the frequency λ_z , which is a weighted average (over the micro-states x , with weights given by the invariant measure π_z) of the frequencies $\overline{C}_{z,1-z}(x)$. In turn, these frequencies are the transition frequencies from the micro-state x of the macro-state z to the other macro-state.

As already emphasized in the introduction, we point out that the above theorem states a convergence result on the *path* $(Z_t^\epsilon)_{t \geq 0}$, and not only of the random variable Z_t^ϵ at any time t .

2.2 Proofs

To simplify the notation, we first consider the case when both macro-states are similar: in that case, $Q_0 = Q_1 = Q$ and $C_{0,1} = C_{1,0} = C$. The proof of Theorem 2.3 is performed in Section 2.2.2, and uses some intermediate results shown in Section 2.2.1. We briefly mention in Section 2.2.3 how to adapt the proof to handle the general case.

The following computation will be very useful in what follows. Recall that the generator of the process Y_t^ϵ is given by

$$\begin{aligned} L^\epsilon \varphi(x, z) = & \sum_{x' \in M} \epsilon^{-1} Q(x, x') (\varphi(x', z) - \varphi(x, z)) \\ & + \sum_{x' \in M} C(x, x') (\varphi(x', 1-z) - \varphi(x, z)). \end{aligned}$$

We refer the reader to the textbook [4, Section 4.2] for more details on semi-groups and generators associated to jump processes.

Taking $\varphi(x, z) = 1_{z=1}(x, z)$ in the above relation, we obtain

$$L^\epsilon 1_{z=1}(x, z) = - \sum_{x' \in M} C(x, x') 1_{z=1}(x, z) + \sum_{x' \in M} C(x, x') 1_{z=0}(x, z),$$

and thus, taking $(x, z) = Y_t^\epsilon = (X_t^\epsilon, Z_t^\epsilon)$, we have

$$L^\epsilon 1_{z=1}(Y_t^\epsilon) = \sum_{x' \in M} C(X_t^\epsilon, x') (1 - 2Z_t^\epsilon) = \overline{C}(X_t^\epsilon) (1 - 2Z_t^\epsilon)$$

where $\overline{C}(x) = \sum_{x' \in M} C(x, x')$. We now define the process $(M_t^\epsilon)_{t \geq 0}$ by

$$\begin{aligned} M_t^\epsilon &= 1_{z=1}(Y_t^\epsilon) - 1_{z=1}(Y_0^\epsilon) - \int_0^t L^\epsilon 1_{z=1}(Y_s^\epsilon) ds \\ &= Z_t^\epsilon - Z_0 - \int_0^t \sum_{x' \in M} C(X_s^\epsilon, x') (1 - 2Z_s^\epsilon) ds. \end{aligned} \quad (5)$$

Using Proposition A.1, we see that M_t^ϵ is a martingale with respect to the filtration $\mathcal{F}_t^\epsilon = \sigma(Y_s^\epsilon, s \leq t)$, and that its quadratic variation is given by

$$\begin{aligned} \langle M^\epsilon \rangle_t &= \int_0^t (L^\epsilon 1_{z=1}(Y_s^\epsilon) - 2 1_{z=1}(Y_s^\epsilon) L^\epsilon 1_{z=1}(Y_s^\epsilon)) ds \\ &= \int_0^t \overline{C}(X_s^\epsilon) (1 - 2Z_s^\epsilon) - 2Z_s^\epsilon \overline{C}(X_s^\epsilon) (1 - 2Z_s^\epsilon) ds \\ &= \int_0^t \overline{C}(X_s^\epsilon) (1 - 2Z_s^\epsilon)^2 ds \\ &= \int_0^t \overline{C}(X_s^\epsilon) ds \\ &= \int_0^t g(X_s^\epsilon) ds + \lambda t, \end{aligned} \quad (6)$$

where $\lambda = \lambda_0 = \lambda_1$ (see (3)) and

$$g(x) = \overline{C}(x) - \lambda = \sum_{x' \in M} C(x, x') - \lambda. \quad (7)$$

We have used in the above computation the fact that $(1 - 2Z_s^\epsilon)^2 = 1$, a direct consequence of the fact that $Z_s^\epsilon = 0$ or 1 .

In what follows, we will use the fact that

$$Z_t^\epsilon = Z_0 + \int_0^t f(Y_s^\epsilon) ds + \int_0^t \lambda (1 - 2Z_s^\epsilon) ds + M_t^\epsilon \quad (8)$$

with

$$f(x, z) = \left(\sum_{x' \in M} C(x, x') - \lambda \right) (1 - 2z), \quad (9)$$

which is a straightforward reformulation of (5).

2.2.1 Some intermediate results

The following results are useful in the proof of Theorem 2.3.

Lemma 2.4. *Let L be a $m \times m$ matrix and let $x \in \mathbb{R}^m$. Assume that for any $y \in \mathbb{R}^m$ such that $y^T L = 0$, we have $y^T x = 0$. Then, there exists $z \in \mathbb{R}^m$ such that $Lz = x$.*

Proof. We denote by C_1, \dots, C_m the columns of the matrix L and by $V = \text{Span}\{C_1, \dots, C_m\}$. The assumption on x is that $x \in (V^\perp)^\perp = V$. Therefore, x can be written in the form $x = \sum_{i=1}^m \alpha_i C_i$ for some coefficients $(\alpha_i)_{1 \leq i \leq m}$. Let $z = \sum_{i=1}^m \alpha_i e_i$, with $(e_i)_{1 \leq i \leq m}$ the canonical basis of \mathbb{R}^m . We check that z satisfies $Lz = x$. \square

Lemma 2.5. *Let $F = \{0, 1\}$, Z_0 be a random variable valued in F , $\lambda_0, \lambda_1 \geq 0$, and $(Z_t)_{t \geq 0}$ be a stochastic process on F . If the process*

$$M_t = Z_t - Z_0 - \int_0^t (\lambda_0 - (\lambda_0 + \lambda_1) Z_s) ds$$

is a martingale with respect to the natural filtration of $(Z_t)_{t \geq 0}$, then $(Z_t)_{t \geq 0}$ is a Markov jump process of initial condition Z_0 and of intensity matrix given by

$$R = \begin{pmatrix} 0 & \lambda_0 \\ \lambda_1 & 0 \end{pmatrix}. \quad (10)$$

Proof. We use the uniqueness result of the martingale problem associated to the Markov jump process with intensity matrix R introduced by D.W. Stroock and S.R.S. Varadhan (see e.g. [8, Theorem 21.11]). We recall a simple version of that result in Lemma A.2 below. In view of that result, we only need to check that, for any bounded function $\varphi : F \mapsto \mathbb{R}$, the process

$$M_t^\varphi = \varphi(Z_t) - \varphi(Z_0) - \int_0^t L\varphi(Z_s) ds$$

is a martingale, where L is the generator of the jump process associated to the intensity matrix (10), which reads

$$L\varphi(z) = \sum_{z' \in F} R(z, z') (\varphi(z') - \varphi(z)).$$

We note that

$$L\varphi(z=0) = \lambda_0 (\varphi(1) - \varphi(0)), \quad L\varphi(z=1) = \lambda_1 (\varphi(0) - \varphi(1)).$$

Since $F = \{0, 1\}$, any bounded function $\varphi : F \mapsto \mathbb{R}$ is of the form

$$\forall z \in F, \quad \varphi(z) = a\delta_{0z} + b\delta_{1z} = a + (b - a)\delta_{1z},$$

for some a and b , where δ_{1z} is the Kronecker symbol. The application $\varphi \mapsto M_t^\varphi$ is obviously linear, and it vanishes for constant functions. Therefore, to show that M_t^φ is a martingale for any bounded function $\varphi : F \mapsto \mathbb{R}$, it is sufficient to show that $M_t^{\delta_{1z}}$ is a martingale. On F , we see that $\delta_{1z} = \text{Id}$. We thus have

$$\begin{aligned} M_t^{\delta_{1z}} &= M_t^{\text{Id}} \\ &= Z_t - Z_0 - \int_0^t L\text{Id}(Z_s) ds \\ &= Z_t - Z_0 - \int_0^t (\lambda_0 - (\lambda_0 + \lambda_1) Z_s) ds. \end{aligned}$$

Using the assumption of the Lemma, we have that $M_t^{\delta_{1z}}$ is a martingale. This concludes the proof. \square

Lemma 2.6. *Let $g : \mathbb{R} \rightarrow \mathbb{R}$ be a Lipschitz function. Then, the function Φ defined by*

$$\begin{aligned} \Phi : D_{\mathbb{R}}[0, \infty) &\rightarrow C_{\mathbb{R}}[0, \infty) \subset D_{\mathbb{R}}[0, \infty) \\ x &\mapsto \left(\int_0^t g(x(s)) ds \right)_t \end{aligned}$$

is continuous.

Proof. Let $(x_n)_{n \in \mathbb{N}}$ be a sequence in $D_{\mathbb{R}}[0, \infty)$ and x in $D_{\mathbb{R}}[0, \infty)$ such that $(x_n)_{n \in \mathbb{N}}$ converges to x in $D_{\mathbb{R}}[0, \infty)$ for the Skorohod topology. We show that $(\Phi(x_n))_{n \in \mathbb{N}}$ converges to $\Phi(x)$ in the Skorohod topology.

We first observe that, for any $y \in D_{\mathbb{R}}[0, \infty)$, the function $\Phi(y)$ is continuous. Since the limit function $\Phi(x)$ is hence continuous, the convergence of $(\Phi(x_n))_{n \in \mathbb{N}}$ to $\Phi(x)$ in the Skorohod topology is equivalent to the convergence of $(\Phi(x_n))_{n \in \mathbb{N}}$ to $\Phi(x)$ according to the norm $\|\cdot\|_{C^0([0, T])}$, on any compact time interval $[0, T]$ (see e.g. [3, p. 124]).

We now proceed and show that, for any $T > 0$, $\|\Phi(x_n) - \Phi(x)\|_{C^0([0, T])}$ goes to zero as n goes to ∞ . Using the characterization of the convergence of $(x_n)_{n \in \mathbb{N}}$ to x given in Proposition A.3, we know that there exists a sequence

of strictly increasing, continuous maps λ_n defined on $[0, \infty)$ satisfying (45) and (46) below. We then have, for any $t \in [0, T]$,

$$\begin{aligned} & |\Phi(x_n)(t) - \Phi(x)(t)| \\ &= \left| \int_0^t (g(x_n(s)) - g(x(s))) ds \right| \\ &\leq \int_0^t |g(x_n(s)) - g(x(\lambda_n(s)))| ds + \int_0^t |g(x(\lambda_n(s))) - g(x(s))| ds \end{aligned} \quad (11)$$

The first term of the right-hand side of (11) tends to 0 as n goes to ∞ uniformly on $[0, T]$. Indeed,

$$\begin{aligned} \sup_{t \in [0, T]} \int_0^t |g(x_n(s)) - g(x(\lambda_n(s)))| ds &\leq T \sup_{s \in [0, T]} |g(x_n(s)) - g(x(\lambda_n(s)))| \\ &\leq T C_g \sup_{s \in [0, T]} |x_n(s) - x(\lambda_n(s))|, \end{aligned}$$

where C_g is the Lipschitz constant of g . Using (46), we deduce that

$$\lim_{n \rightarrow \infty} \sup_{t \in [0, T]} \int_0^t |g(x_n(s)) - g(x(\lambda_n(s)))| ds = 0. \quad (12)$$

We now turn to the second term of the right-hand side of (11). Take $\alpha > 0$. Using [2, Lemma 1 p. 110], we know that there exists a subdivision

$$0 = t_0 < t_1 < \dots < t_r = T$$

of $[0, T]$ such that, for any i ,

$$\sup\{|x(s) - x(t)|, t_i \leq s \leq t \leq t_{i+1}\} \leq \alpha.$$

This result is based on the fact that (i) a continuous function on a compact set is also uniformly continuous on this set, and (ii) for any $\beta > 0$, a càd-làg function on a compact set has a finite number of jumps larger than the threshold β .

Using this subdivision of $[0, T]$, we bound the second term of the right-hand side of (11) by

$$\begin{aligned} \int_0^t |g(x(\lambda_n(s))) - g(x(s))| ds &\leq \sum_{i=0}^{r-1} \int_{t_i}^{t_{i+1}} |g(x(\lambda_n(s))) - g(x(s))| ds \\ &\leq \sum_{i=0}^{r-1} C_g \int_{t_i}^{t_{i+1}} |x(\lambda_n(s)) - x(s)| ds. \end{aligned} \quad (13)$$

Let us introduce $\delta > 0$ such that for any $0 \leq i \leq r-1$, we have $2\delta < t_{i+1} - t_i$. As there is a finite number of points t_i , such a $\delta > 0$ exists. Using the property (45) of λ_n , we know that there exists N such that, for any $n > N$, we have $\sup_{s \in [0, T]} |\lambda_n(s) - s| \leq \delta$. We therefore deduce that, for any $n > N$,

$$\begin{aligned}
& \sum_{i=0}^{r-1} \int_{t_i}^{t_{i+1}} |x(\lambda_n(s)) - x(s)| ds \\
& \leq \sum_{i=0}^{r-1} \int_{t_i+\delta}^{t_{i+1}-\delta} |x(\lambda_n(s)) - x(s)| ds + 4r\delta \sup_{t \in [0, T+\delta]} |x(t)| \\
& \leq \sum_{i=0}^{r-1} (t_{i+1} - t_i - 2\delta) \alpha + 4r\delta \sup_{t \in [0, T+\delta]} |x(t)| \\
& \leq T\alpha + 4r\delta \sup_{t \in [0, T+\delta]} |x(t)|.
\end{aligned} \tag{14}$$

Inserting (14) in (13), we deduce that the second term of the right-hand side of (11) is bounded by

$$\int_0^t |g(x(\lambda_n(s))) - g(x(s))| ds \leq C_g T \alpha + 4C_g r \delta \sup_{t \in [0, T+\delta]} |x(t)|.$$

As α and δ are arbitrary small, and r only depends on α , we conclude that the second term of the right-hand side of (11) converges to 0 uniformly in t on $[0, T]$.

Collecting this result with the limit (12) on the first term and (11), we deduce that

$$\lim_{n \rightarrow \infty} \sup_{t \in [0, T]} |\Phi(x_n)(t) - \Phi(x)(t)| = 0.$$

This concludes the proof of Lemma 2.6. \square

Remark 2.7. *If the function g is not continuous, then Φ is not continuous. Consider indeed a sequence $(x_n)_{n \in \mathbb{N}}$ of real numbers that converges from above to x , a discontinuity point of g . Denoting $\Phi(x_n)$ the image by Φ of the constant function equal to x_n , we see that, for any t ,*

$$\Phi(x_n)(t) - \Phi(x)(t) \longrightarrow t(g(x+) - g(x)) \neq 0.$$

We conclude these intermediate results with the following proposition, that will be useful to study the limit when $\epsilon \rightarrow 0$ of the second term in the right-hand side of (8).

Proposition 2.8. *Let f be given by (9). Under the hypothesis of Theorem 2.3, we have, for any $t \geq 0$,*

$$\mathbb{E} \left[\left(\int_0^t f(Y_s^\epsilon) ds \right)^2 \right] \longrightarrow 0 \quad \text{as } \epsilon \rightarrow 0. \quad (15)$$

Proof. Since E is a finite set, we identify functions $\varphi : E \rightarrow \mathbb{R}$ with the vectors $((\varphi(x, 0))_{x \in M}, (\varphi(x, 1))_{x \in M}) \in \mathbb{R}^{2m}$ throughout the proof. We likewise identify operators with matrices.

Let \overline{L}^0 be the generator corresponding to the intensity matrix \overline{Q}^0 :

$$\overline{L}^0 u(x, z) = \sum_{x' \in M} Q(x, x') (u(x', z) - u(x, z)).$$

First, we claim that

$$\text{there exists a function } u : E \mapsto \mathbb{R} \text{ such that } \overline{L}^0 u = f. \quad (16)$$

Indeed, as Q is irreducible, the only vectors $\mu \in \mathbb{R}^{2m}$ such that $\mu^T \overline{L}^0 = 0$ are the vectors of the form $\mu_{\alpha, \beta} = (\alpha\pi, \beta\pi)$ for any $\alpha, \beta \in \mathbb{R}$ (this is a simple consequence of the Perron-Frobenius theorem). Using (9) and (3), we compute

$$\begin{aligned} \mu_{\alpha, \beta}^T f &= \sum_{x \in M} \alpha \pi(x) f(x, 0) + \sum_{x \in M} \beta \pi(x) f(x, 1) \\ &= (\alpha - \beta) \left(\sum_{x \in M} \pi(x) \sum_{x' \in M} C(x, x') - \lambda \right) \\ &= 0. \end{aligned} \quad (17)$$

We thus see that, for any $\mu \in \mathbb{R}^{2m}$ such that $\mu^T \overline{L}^0 = 0$, we have $\mu^T f = 0$. We are now in position to use Lemma 2.4, from which we deduce the claim (16).

Second, using (16), we write that

$$\begin{aligned} \int_0^t f(Y_s^\epsilon) ds &= \int_0^t \overline{L}^0 u(Y_s^\epsilon) ds \\ &= \epsilon \int_0^t L^\epsilon u(Y_s^\epsilon) - \epsilon \int_0^t L^C u(Y_s^\epsilon) ds \end{aligned} \quad (18)$$

where we have used the decomposition

$$\epsilon L^\epsilon u = \overline{L}^0 u + \epsilon L^C u$$

with

$$L^C u(x, z) = \sum_{x' \in M} C(x, x') (u(x', 1 - z) - u(x, z)).$$

We successively bound the two terms of the right-hand side of (18). Introduce $N_t^u = u(Y_t^\epsilon) - u(Y_0^\epsilon) - \int_0^t L^\epsilon u(Y_s^\epsilon) ds$. In view of Proposition A.1, we know that N_t^u is a martingale of quadratic variation given by

$$\langle N^u \rangle_t = \int_0^t (L^\epsilon u^2(Y_s^\epsilon) - 2u(Y_s^\epsilon) L^\epsilon u(Y_s^\epsilon)) ds.$$

For any $v : E \rightarrow \mathbb{R}$, we have

$$\|L^\epsilon v\|_\infty \leq 2m\|v\|_\infty (\epsilon^{-1}\|Q\|_\infty + \|C\|_\infty).$$

Therefore,

$$\begin{aligned} \mathbb{E} \left[(N_t^u)^2 \right] &= \mathbb{E} (\langle N^u \rangle_t) \\ &\leq 2mt [\|u^2\|_\infty (\epsilon^{-1}\|Q\|_\infty + \|C\|_\infty) + 2\|u\|_\infty^2 (\epsilon^{-1}\|Q\|_\infty + \|C\|_\infty)] \\ &\leq A + \epsilon^{-1}B, \end{aligned}$$

where A and B are positive constants independent of ϵ . It follows that the first term of the right hand side of (18) satisfies

$$\begin{aligned} \mathbb{E} \left[\left(\epsilon \int_0^t L^\epsilon u(Y_s^\epsilon) \right)^2 \right] &= \mathbb{E} \left[(\epsilon (N_t^u - u(Y_t^\epsilon) + u(Y_0^\epsilon)))^2 \right] \\ &\leq 2\epsilon^2 \left(\mathbb{E} \left[(N_t^u)^2 \right] + 4\|u^2\|_\infty \right) \\ &\leq 2\epsilon^2 (A' + \epsilon^{-1}B). \end{aligned} \tag{19}$$

For the second term of the right hand side of (18), we directly obtain

$$\mathbb{E} \left[\left(\epsilon \int_0^t L^C u(Y_s^\epsilon) \right)^2 \right] \leq \epsilon^2 t^2 (4m\|C\|_\infty^2 \|u\|_\infty^2). \tag{20}$$

Collecting (18), (19) and (20), we obtain the desired result (15). This concludes the proof of Proposition 2.8. \square

2.2.2 Proof of Theorem 2.3 (symmetric case)

All the convergences in this proof are taken when ϵ goes to 0. We will omit to recall it. The proof consists of four steps.

Step 1: the family of probability measures $(\mathcal{P}^\epsilon)_{\epsilon>0}$ is relatively compact

We use the tightness criterion of Theorem A.4, and check that its conditions (47) and (48) are satisfied.

As the variables Z_t^ϵ take only two values, 0 and 1, the condition (47) is trivially satisfied with the choices $K = 1$ and $n_0 = 1$.

Let us now show that the condition (48) is satisfied. Let $N \in \mathbb{N}$, $\alpha > 0$, $\theta > 0$ and $\epsilon > 0$. Let S and T be two \mathcal{F}^ϵ -stopping times such that $S \leq T \leq S + \theta \leq N$. Recall that a random variable $T : (\Omega, (\mathcal{F}_t)_{t \geq 0}) \rightarrow \mathbb{R}^+ \cup \{\infty\}$ is a stopping time if, for any $t \geq 0$, the set $\{T \leq t\}$ is \mathcal{F}_t -measurable. Using (5), we have

$$|Z_T^\epsilon - Z_S^\epsilon| \leq \left| \int_S^T \sum_{y \in M} C(X_s^\epsilon, y) (1 - 2Z_s^\epsilon) ds \right| + |M_T^\epsilon - M_S^\epsilon|. \quad (21)$$

The first term of the right-hand side of (21) is bounded as follows:

$$\left| \int_S^T \sum_{y \in M} C(X_s^\epsilon, y) (1 - 2Z_s^\epsilon) ds \right| \leq |T - S| m \|C\|_\infty \leq \theta m \|C\|_\infty. \quad (22)$$

To bound the second term of the right-hand side of (21), we use the Tchebychev inequality:

$$\mathbb{P}(|M_T^\epsilon - M_S^\epsilon| \geq \alpha) \leq \frac{\mathbb{E}|M_T^\epsilon - M_S^\epsilon|^2}{\alpha^2}. \quad (23)$$

We denote by $\widetilde{M}_t^\epsilon = M_{t+S}^\epsilon - M_S^\epsilon$ and $\widetilde{\mathcal{F}}_t^\epsilon = \mathcal{F}_{t+S}^\epsilon$. As S is a bounded stopping time, we infer from the optional stopping theorem (see e.g. [16, Theorem 3.2]) that \widetilde{M}^ϵ is a $\widetilde{\mathcal{F}}^\epsilon$ -martingale, of quadratic variation

$$\langle \widetilde{M}^\epsilon \rangle_t = \langle M^\epsilon \rangle_{S+t} - \langle M^\epsilon \rangle_S.$$

In particular, we have

$$\langle \widetilde{M}^\epsilon \rangle_{T-S} = \langle M^\epsilon \rangle_T - \langle M^\epsilon \rangle_S.$$

It follows that

$$\begin{aligned}
\mathbb{E} [|M_T^\epsilon - M_S^\epsilon|^2] &= \mathbb{E} [\widetilde{M}_{T-S}^\epsilon]^2 \\
&= \mathbb{E} [\langle \widetilde{M}^\epsilon \rangle_{T-S}] \\
&= \mathbb{E} [\langle M^\epsilon \rangle_T - \langle M^\epsilon \rangle_S] \\
&= \mathbb{E} \left[\int_S^T g(X_s^\epsilon) ds + \lambda(T - S) \right] \\
&\leq \theta(\|g\|_\infty + \lambda),
\end{aligned} \tag{24}$$

where we have used (6) and where g is defined by (7). We then infer from (23) that

$$\mathbb{P}(|M_T^\epsilon - M_S^\epsilon| \geq \alpha) \leq \frac{\theta(\|g\|_\infty + \lambda)}{\alpha^2}. \tag{25}$$

We deduce from (21), (22) and (25) that the condition (48) of Theorem A.4 below is satisfied.

Assumptions (47) and (48) being satisfied, we can apply Theorem A.4, which implies that the family of probability measures $(\mathcal{P}^\epsilon)_\epsilon$ is tight. In view of Prohorov's theorem (see e.g. [4, Theorem 2.2]), this implies that the family $(\mathcal{P}^\epsilon)_{\epsilon > 0}$ is relatively compact.

There thus exists a sub-family of $(\mathcal{P}^\epsilon)_\epsilon$, that we denote $(\mathcal{P}^{\epsilon'})_{\epsilon'}$, which is convergent. Otherwise stated, there exists a process Z such that $Z^{\epsilon'} \Rightarrow Z$.

Step 2: there exists a martingale M_t and a sub-family $M_t^{\epsilon'}$ such that $M_t^{\epsilon'} \Rightarrow M_t$

In view of [7, Theorem VI.4.13], a sufficient criterion for (M^ϵ) to be relatively compact is that $(\langle M^\epsilon \rangle)$ is C-tight. Let us check this criterion. We have shown above (see (6)) that

$$\langle M^\epsilon \rangle_t = \int_0^t g(X_s^\epsilon) ds + \lambda t,$$

where g is defined by (7). Therefore, the family of paths $(\langle M^\epsilon \rangle)_{\epsilon > 0}$ is uniformly Lipschitz, and hence C-tight (see [7, Definition VI.3.25 and Proposition VI.3.26]). We can thus consider a sub-family of $(M_t^\epsilon)_{t \geq 0}$, that we denote $(M_t^{\epsilon'})_{t \geq 0}$, which weakly converges to a process M . Using [7, Proposition IX.1.1], we know that the process $(M_t)_{t \geq 0}$ is a martingale with respect to its natural filtration.

Step 3: equation satisfied by Z

We have shown at the end of Step 1 that there exists a process Z and a sub-family $Z^{\epsilon'}$ such that $Z^{\epsilon'} \Rightarrow Z$. We now identify a stochastic differential equation satisfied by $(Z_t)_{t \geq 0}$.

Recall first that $(Z_t^\epsilon)_{t \geq 0}$ satisfies (8), namely

$$Z_t^\epsilon = Z_0 + \int_0^t f(Y_s^\epsilon) ds + \int_0^t \lambda(1 - 2Z_s^\epsilon) ds + M_t^\epsilon. \quad (26)$$

Passing to the limit $\epsilon' \rightarrow 0$, let us show that $(Z_t)_{t \geq 0}$ satisfies

$$Z_t = Z_0 + \int_0^t \lambda(1 - 2Z_s) ds + M_t. \quad (27)$$

We first consider $B_t^\epsilon = \int_0^t f(Y_s^\epsilon) ds$. With the same techniques as above, we can show that (B_t^ϵ) is a relatively compact family. There thus exists (B_t) and a sub-family $(B_t^{\epsilon'})$ such that $B^{\epsilon'} \Rightarrow B$. We infer from Proposition 2.8 that, for all $t \geq 0$, B_t^ϵ converges to 0 in $L^2(\Omega)$, hence $\mathbb{E}[B_t^2] = 0$ for all $t \geq 0$. It follows that the family $(B_t^{\epsilon'})$ converges to 0 in distribution.

We next turn to $J_t^\epsilon = \int_0^t \lambda(1 - 2Z_s^\epsilon) ds$. Introduce $J_t = \int_0^t \lambda(1 - 2Z_s) ds$. The function $g : z \mapsto \lambda(1 - 2z)$ is Lipschitz on \mathbb{R} , thus, using Lemma 2.6, we know that the function

$$\begin{aligned} \Phi : D_{\mathbb{R}}[0, \infty) &\longrightarrow D_{\mathbb{R}}[0, \infty) \\ z &\longmapsto \left(\int_0^t \lambda(1 - 2z(s)) ds \right)_t \end{aligned}$$

is continuous. The convergence $Z^{\epsilon'} \Rightarrow Z$ therefore implies that

$$J^{\epsilon'} = \Phi(Z^{\epsilon'}) \Rightarrow \Phi(Z) = J.$$

We have thus obtained that all the terms in (26) weakly converge. It remains to show that we can add up the weak limits. To do so, we show with the same techniques as before that the family $(B^\epsilon, J^\epsilon, M^\epsilon)$ is relatively compact, and that the limit of any sub-family has as marginal distributions those of B , J and M . We conclude that $B^{\epsilon'} + J^{\epsilon'} + M^{\epsilon'} \Rightarrow B + J + M$. Passing to the limit $\epsilon' \rightarrow 0$ in (26), we then indeed obtain (27).

Step 4: conclusion

We infer from (27) (where, we recall, M_t is a martingale) and Lemma 2.5 (with $\lambda_0 = \lambda_1 = \lambda$) that $(Z_t)_{t \geq 0}$ is a Markov jump process of initial condition Z_0 and of intensity matrix given

$$\begin{pmatrix} 0 & \lambda \\ \lambda & 0 \end{pmatrix}.$$

The process Z is thus uniquely defined.

It follows that all convergent sub-families $Z^{\epsilon'}$ have the same limit Z . The whole sequence Z^ϵ therefore converges to this common limit Z . This concludes the proof of Theorem 2.3 in the symmetric case.

2.2.3 Non-symmetric case

In this Section, we briefly sketch the proof in the non-symmetric case, that is when $Q_0 \neq Q_1$ or $C_{0,1} \neq C_{1,0}$ in (1). The structure of the proof is similar to that in the symmetric case.

First, the generator associated to the process (Y_t^ϵ) reads

$$\begin{aligned} L^\epsilon \varphi(x, z) = & \sum_{x' \in M} \epsilon^{-1} Q_z(x, x') (\varphi(x', z) - \varphi(x, z)) \\ & + \sum_{x' \in M} C_{z, 1-z}(x, x') (\varphi(x', 1-z) - \varphi(x, z)). \end{aligned}$$

Choosing the function $\varphi(x, z) = z$, we see that

$$L^\epsilon \varphi(x, z) = \sum_{x' \in M} C_{z, 1-z}(x, x') (1 - 2z) = f(x, z) + h(z),$$

where we have introduced (recall (3))

$$f(x, z) = \left(\sum_{x' \in M} C_{z, 1-z}(x, x') - \lambda_z \right) (1 - 2z)$$

and

$$h(z) = (1 - 2z)\lambda_z = (1 - 2z) \sum_{x, x' \in M} C_{z, 1-z}(x, x') \pi_z(x).$$

Using again Proposition A.1, we see that the process

$$M_t^\epsilon = \varphi(Y_t^\epsilon) - \varphi(Y_0^\epsilon) - \int_0^t L^\epsilon \varphi(Y_s^\epsilon) ds \quad (28)$$

is a martingale. Using the above notation, the equation (28) can be recast as

$$Z_t^\epsilon = Z_0 + \int_0^t f(Y_s^\epsilon) ds + \int_0^t h(Z_s^\epsilon) ds + M_t^\epsilon. \quad (29)$$

To pass to the limit $\epsilon \rightarrow 0$ in the above equation, we follow the same lines as in the proof detailed in Sections 2.2.1 and 2.2.2.

Consider the second term of the right-hand side of (29). As in the proof of Proposition 2.8, we can show that $\mu^T f = 0$ for any $\mu \in \mathbb{R}^{2m}$ such that $\mu^T \bar{L}^0 = 0$, which are vectors of the form $(\alpha\pi_0, \beta\pi_1)$ for any α and β in \mathbb{R} . This implies that $\int_0^t f(Y_s^\epsilon) ds$ converges to 0 in $L^2(\Omega)$ for any $t \geq 0$.

We turn now to the third term of the right-hand side of (29). Let \tilde{h} be the affine function defined on \mathbb{R} by $\tilde{h}(0) = h(0)$ and $\tilde{h}(1) = h(1)$. The function \tilde{h} is obviously Lipschitz on \mathbb{R} , hence, using Lemma 2.6, we know that the function

$$\begin{aligned} \Phi : D_{\mathbb{R}}[0, \infty) &\rightarrow D_{\mathbb{R}}[0, \infty) \\ z &\mapsto \left(\int_0^t \tilde{h}(z(s)) ds \right)_t \end{aligned}$$

is continuous. Since $\int_0^t h(Z_s^\epsilon) ds = \int_0^t \tilde{h}(Z_s^\epsilon) ds$, this allows to pass to the limit in that term.

As in Section 2.2.2 (Step 3 of the proof), we can thus pass to the limit $\epsilon \rightarrow 0$ in (29), and show that Z^ϵ converges in distribution to a process Z , that satisfies

$$\begin{aligned} Z_t &= Z_0 + \int_0^t h(Z_s) ds + M_t \\ &= Z_0 + \int_0^t [\lambda_0 - Z_s(\lambda_0 + \lambda_1)] ds + M_t, \end{aligned}$$

where M is a martingale. We then infer from Lemma 2.5 that $(Z_t)_{t \geq 0}$ is a jump process on $\{0, 1\}$, of initial condition Z_0 and of intensity matrix

$$\begin{pmatrix} 0 & \lambda_0 \\ \lambda_1 & 0 \end{pmatrix},$$

as claimed in Theorem 2.3.

2.3 Numerical illustration

We have implemented the model presented in Section 2.1. As shown on Fig. 1, the energy wells can be gathered in two macro-states (each of them containing m micro-states) separated by a high potential energy barrier. The transitions are only possible from one well to its two nearest neighbours. In addition, we apply periodic boundary conditions. The matrices Q_0 , Q_1 , $C_{0,1}$ and $C_{1,0}$ of the intensity matrix (1) read

$$Q_0 = Q_1 = Q \quad \text{and} \quad C_{0,1} = C_{1,0} = C$$

with

$$Q = \begin{pmatrix} 0 & q & & & \\ q & 0 & q & & \\ \cdot & \cdot & \cdot & \cdot & \\ & & & q & 0 & q \\ & & & q & 0 & \end{pmatrix}, \quad C = \begin{pmatrix} 0 & \cdots & & 0 & c \\ 0 & \cdots & & & 0 \\ \vdots & & & & \vdots \\ c & 0 & \cdots & & 0 \end{pmatrix}.$$

We work with $q = c = 1$.

We are interested in the distribution of the first exit time S_0^ϵ from a macro-state. From Theorem 2.3, we know that, in the limit ϵ going to 0, S_0^ϵ follows an exponential distribution of parameter $\lambda = 2c/m$ (independently of what the initial condition of the system is). In order to quantify the convergence of the distribution of S_0^ϵ to the predicted distribution, we consider the L^1 norm of the difference of the densities:

$$\text{err}_{L^1} = \int_0^\infty |f - f^\epsilon| \approx \frac{1}{n} \sum_{i=1}^n |f(i\Delta x) - f_i^\epsilon|, \quad (30)$$

where $f(x) = \lambda e^{-\lambda x}$ is the limit distribution and f^ϵ is the distribution of S_0^ϵ . This latter distribution is calculated on the bounded interval $[0, s]$ with

$s = n\Delta x$ on a grid of size Δx : $f_i^\epsilon \approx \frac{1}{\Delta x} \sum_{x \in [i\Delta x, (i+1)\Delta x]} f^\epsilon(x)$ for any $i \in [1, n]$.

In the sequel, we work with $\Delta x = 0.05$ and $s = n\Delta x = 5$.

Remark 2.9. *Other criteria can also be considered to characterize the convergence of the probability distribution f^ϵ towards f . One example is the discrepancy, which is the difference (in L^∞ norm) of the cumulative distribution functions:*

$$D = \sup_{A \geq 0} \left| \int_0^A f - \int_0^A f^\epsilon \right|. \quad (31)$$

We have used this criterion e.g. on Fig. 5 below.

We first consider how results depend on ϵ . We work with a fixed initial condition, namely $Y_0 = (0, 0)$. At the initial time, the particle is in the first macro-state, and in the micro-state which is the closest to the energy barrier between the two macro-states (see Fig. 1).

On Figs. 2 and 3, we show the convergence of the empirical expectation and variance of S_0^ϵ to the asymptotic value (we have considered 10^4 independent and identically distributed realizations of the process to compute 95 % confidence intervals). We indeed observe convergence of both quantities to their asymptotic limits when $\epsilon \rightarrow 0$.

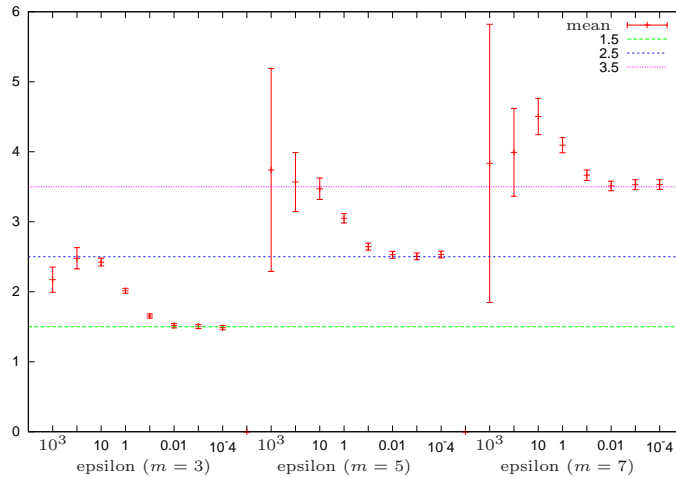


Figure 2: Empirical expectation of S_0^ϵ as a function of ϵ , for $m = 3$ (left), $m = 5$ (middle) and $m = 7$ (right). The asymptotic values (when $\epsilon \rightarrow 0$) are also represented (solid lines).

On Fig. 4, we show the histogram of S_0^ϵ in the case $m = 20$ for two values of ϵ . We again observe a good qualitative agreement with the limit distribution for small enough ϵ . This can be quantified by looking precisely at the convergence of the distribution of S_0^ϵ to the asymptotic distribution when ϵ goes to 0, for different values of m (see Fig. 5). The left part of that figure seems to show that the convergence slows down when the number m of micro-states within a macro-state increases.

We next monitor how the distribution of S_0^ϵ behaves when we vary the initial condition. For this test, we work with $m = 5$. Figures 6 and 7 show the empirical expectation and variance for different initial positions and for

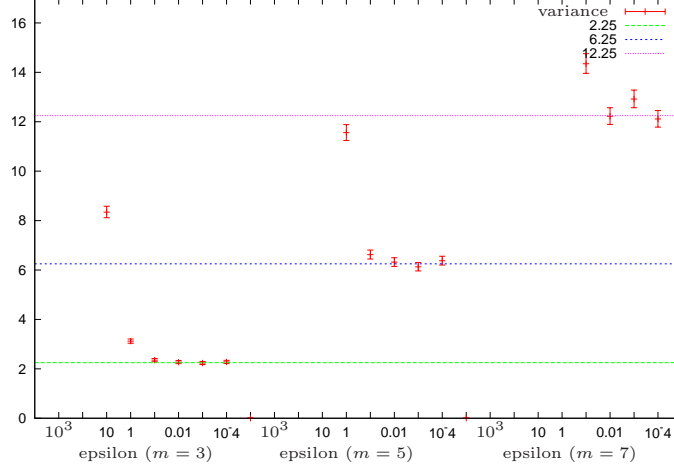


Figure 3: Empirical variance of S_0^ϵ as a function of ϵ , for $m = 3$ (left), $m = 5$ (middle) and $m = 7$ (right). The asymptotic values (when $\epsilon \rightarrow 0$) are also represented (solid lines).

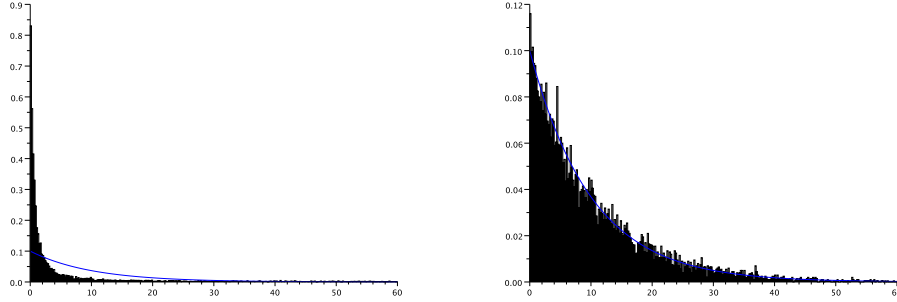


Figure 4: Distribution of S_0^ϵ , the first exit time from a macro-state ($m = 20$). Left: large $\epsilon = 1$. Right: small $\epsilon = 10^{-3}$.

different values of ϵ . We notice that, for an initial condition which is at the middle of the macro-state, the convergence with respect to ϵ is slower than for the initial conditions which are at the boundaries. This difference is due to the diffusion phenomenon which occurs inside each macro-state as a result of the transition to the nearest neighbours.

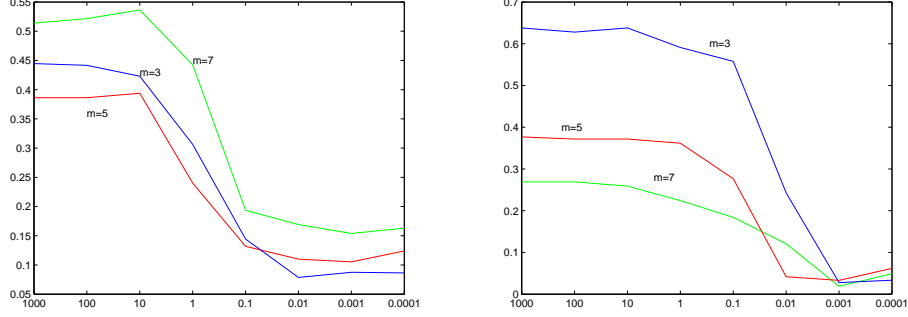


Figure 5: L^1 error (30) (left) and discrepancy (31) (right) on the distribution of S_0^ϵ as a function of ϵ .

To better understand the behavior of the system for large values of m , we have simulated our model with $m = 20$. We show on Figs. 8 and 9 the empirical expectation and variance of S_0^ϵ for two different initial conditions, one on the boundary ($Y_0 = (0, 0)$) and the other in the middle of the macro-state ($Y_0 = (10, 1)$). On Fig. 10, we show the convergence of the distribution of S_0^ϵ to its limit for these two initial conditions.

We clearly see that the convergence is slower and the error margins are larger (for the same number of Monte-Carlo realizations) than when we chose smaller values of m (compare for example Fig. 8 with Fig. 2 or Fig. 10 with Fig. 5). The system indeed takes more time in a given macro-state before reaching its boundary and possibly jumping.

To conclude this numerical illustration, we have monitored the distribution of S_1^ϵ , the exit time from the second macro state, and compared it with that of S_0^ϵ , the exit time from the first macro-state. We observe (results not shown) that S_1^ϵ has the same asymptotic behaviour as S_0^ϵ , a fact which is in agreement with the theoretical predictions.

Remark 2.10. *The parameters of the numerical simulations reported here have been chosen so that the limit dynamics (at $\epsilon = 0$) is an inaccurate approximation of the reference dynamics when ϵ is large (say $\epsilon \geq 1$).*

There are actually cases when the limit dynamics is an accurate approximation of the reference dynamics, even if ϵ is not small. For example, consider the case where, for a given macro-state (say $Z = 0$), the transitions from each micro-state of this macro-state to any micro-state of the other macro-state ($Z = 1$) share the same frequency. In the case of the symmetric

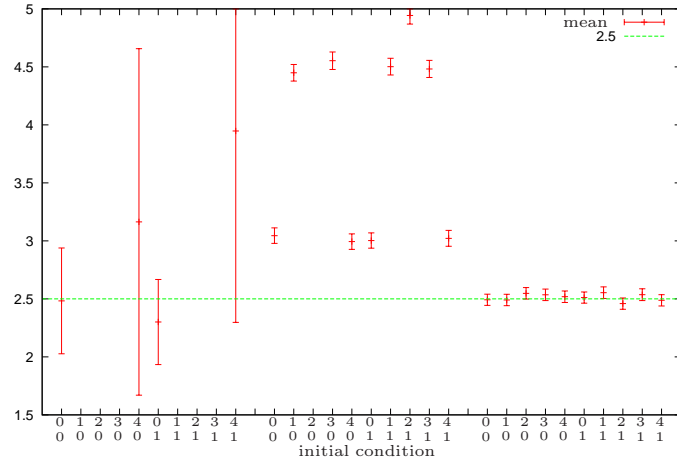


Figure 6: Empirical expectation of S_0^ϵ for different initial conditions and for $\epsilon = 10^3$ (left), $\epsilon = 1$ (center) and $\epsilon = 10^{-3}$ (right). Initial conditions are shown on the x-axis in the format $\begin{pmatrix} X_0 \\ Z_0 \end{pmatrix} \in \begin{pmatrix} M \\ \{0,1\} \end{pmatrix}$, with $M = \{0, 1, 2, 3, 4\}$.

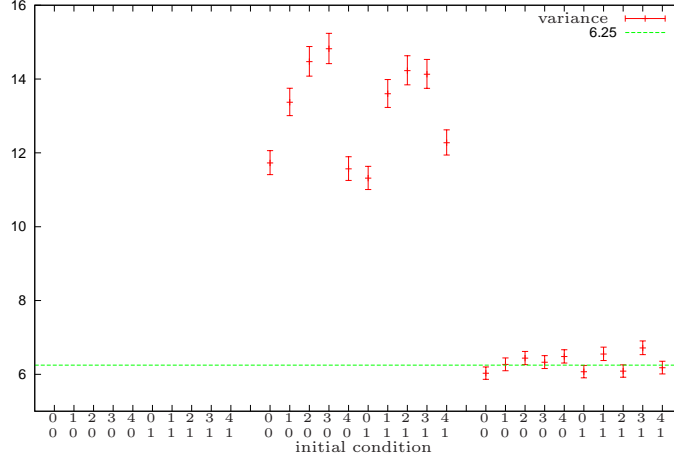


Figure 7: Empirical variance of S_0^ϵ for different initial conditions and different values of ϵ , with the same convention as on Fig. 6 (results for $\epsilon = 10^3$ do not fit in the chosen y-range).

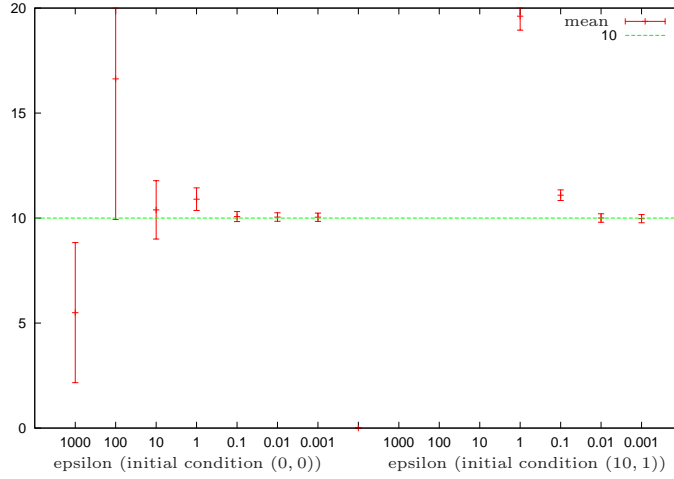


Figure 8: Empirical expectation of S_0^ϵ for $m=20$ and two different initial conditions: $Y_0 = (0,0)$ (left) and $Y_0 = (10,1)$ (right).

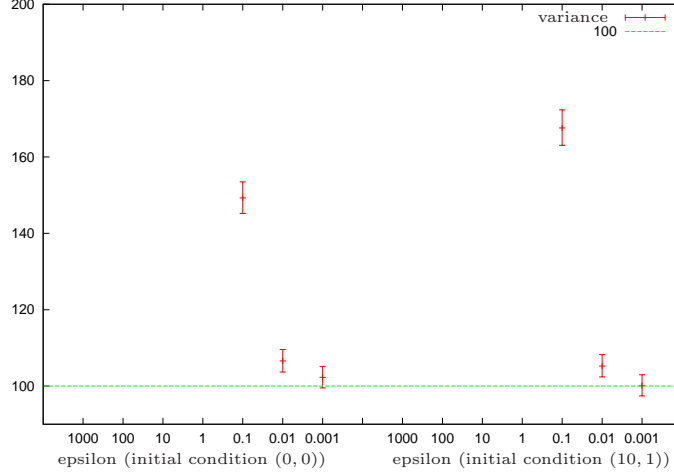


Figure 9: Empirical variance of S_0^ϵ for $m = 20$ and two different initial conditions: $Y_0 = (0, 0)$ (left) and $Y_0 = (10, 1)$ (right).

model considered in Section 2.2, the homogeneity condition means that

$$\sum_{x' \in M} C(x, x') = Cte \text{ independent of } x.$$

In this case, the macroscopic dynamic is decoupled from the microscopic variable, as can be seen from (5), and of course does not depend on ϵ .

3 A particle in a potential energy landscape with infinitely many macro-states

In Section 2, we have studied the dynamics of a particle in a potential energy with two macro-states. We now turn to the system composed of a particle in a potential energy with infinitely many macro-states. We establish a convergence result on the dynamics of a slow quantity of interest in Section 3.1, before turning to numerical illustrations in Section 3.2.

3.1 Presentation of the model and main result

As mentioned above, we consider here the dynamics of a particle in a potential energy with infinitely many macro-states. As in Section 2.1, the state of

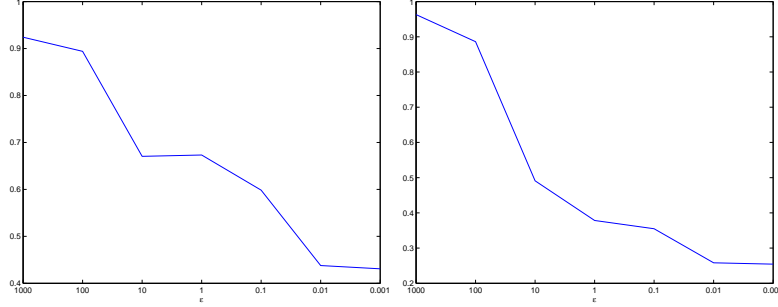


Figure 10: L^1 error (30) on the distribution of S_0^ϵ for $m = 20$. Left: initial condition $Y_0 = (0, 0)$. Right: initial condition $Y_0 = (10, 1)$.

the particle is described by $\overline{Y}_t^\epsilon = (\overline{X}_t^\epsilon, \overline{Z}_t^\epsilon)$, which takes its values in $M \times \mathbb{Z}$, where again $\overline{X}_t^\epsilon \in M = \{1, \dots, m\}$ is the label of the micro-state in which the particle is. The variable \overline{Z}_t^ϵ is the label of the macro-state in which the particle is at time t , and it now takes any value of \mathbb{Z} .

For simplicity, we assume that the dynamics within each macro-state is similar. We also restrict the transitions from one macro-state to its two neighbors. The transition from z to $z + 1$ may have different properties than the transition from z to $z - 1$ (thus creating a macroscopic drift in the dynamics). We also assume that the system is macroscopically homogeneous, in the sense that properties are translation invariant with respect to z . Under these assumptions, a typical transition intensity for the process $(\overline{Y}_t^\epsilon)_t$ is given by

$$\begin{aligned} \forall z \in \mathbb{Z}, \quad \overline{Q}^\epsilon((x, z), (x', z)) &= Q(x, x'), \\ \forall z \in \mathbb{Z}, \quad \overline{Q}^\epsilon((x, z), (x', z + 1)) &= \epsilon C_r(x, x'), \\ \forall z \in \mathbb{Z}, \quad \overline{Q}^\epsilon((x, z), (x', z - 1)) &= \epsilon C_l(x, x'), \\ \forall z \in \mathbb{Z}, \quad \overline{Q}^\epsilon((x, z), (x', z')) &= 0 \text{ if } z' \neq z, z + 1 \text{ or } z - 1. \end{aligned} \quad (32)$$

We again assume that the matrix Q is irreducible (see (2)) and introduce its unique invariant measure π . The average of the jump frequency according to the invariant measure reads

$$\lambda_l = \sum_{x, x' \in M} C_l(x, x') \pi(x), \quad \lambda_r = \sum_{x, x' \in M} C_r(x, x') \pi(x). \quad (33)$$

We introduce the generator L defined by: for any bounded function φ on \mathbb{Z} ,

$$L\varphi(z) = \lambda_l \varphi(z - 1) + \lambda_r \varphi(z + 1) - (\lambda_r + \lambda_l) \varphi(z), \quad (34)$$

which is the generator of a jump process $(Z_t)_{t \geq 0}$ on \mathbb{Z} , with jumps at times defined by a Poisson process of parameter $\lambda_l + \lambda_r$. When the process jumps, it jumps to the right (resp. to the left) with probability $\frac{\lambda_r}{\lambda_r + \lambda_l}$ (resp. $\frac{\lambda_l}{\lambda_r + \lambda_l}$).

The main result of this section is the following:

Theorem 3.1. *Assume that the matrix Q is irreducible. Consider the rescaled-in-time process $Y_t^\epsilon = (X_t^\epsilon, Z_t^\epsilon) = \bar{Y}_{t/\epsilon}^\epsilon$ with initial condition $Y_0 = (X_0, Z_0)$ independent of ϵ . We denote by \mathcal{P}^ϵ the distribution of the process $(Z_t^\epsilon)_t$ and by \mathcal{P} the distribution of the process starting from the initial condition Z_0 and having as generator the operator L defined by (34). Then*

$$\mathcal{P}^\epsilon \Rightarrow \mathcal{P} \text{ as } \epsilon \text{ goes to } 0.$$

The proof of this result follows the same steps as that of Theorem 2.3, up to the fact that the process Z^ϵ is no longer bounded. To circumvent this difficulty, we need to work with an *arbitrary* bounded function of Z^ϵ , in contrast to the proof of Theorem 2.3, where it is sufficient to directly work with Z^ϵ .

We briefly sketch the proof of Theorem 3.1. The generator L^ϵ of Y_t^ϵ reads, for a bounded function φ ,

$$\begin{aligned} L^\epsilon \varphi(x, z) &= \sum_{x' \in M} \epsilon^{-1} Q(x, x') (\varphi(x', z) - \varphi(x, z)) \\ &\quad + \sum_{x' \in M} C_l(x, x') (\varphi(x', z-1) - \varphi(x, z)) \\ &\quad + \sum_{x' \in M} C_r(x, x') (\varphi(x', z+1) - \varphi(x, z)). \end{aligned}$$

For a function $\varphi(x, z) = F(z)$ which only depends on the macroscopic variable (where F is a bounded function on \mathbb{Z}), we have

$$\begin{aligned} (L^\epsilon F)(x, z) &= \sum_{x' \in M} C_l(x, x') (F(z-1) - F(z)) \\ &\quad + \sum_{x' \in M} C_r(x, x') (F(z+1) - F(z)). \end{aligned}$$

Using Proposition A.1, we know that the process

$$M_t^\epsilon = F(Z_t^\epsilon) - F(Z_0) - \int_0^t (L^\epsilon F)(X_s^\epsilon, Z_s^\epsilon) ds \quad (35)$$

is a \mathcal{F}_t^ϵ -martingale. We now introduce

$$\begin{aligned} G(F)(x, z) = & (F(z-1) - F(z)) \sum_{x' \in M} (C_l(x, x') - \lambda_l) \\ & + (F(z+1) - F(z)) \sum_{x' \in M} (C_r(x, x') - \lambda_r), \end{aligned} \quad (36)$$

so that

$$(L^\epsilon F)(x, z) = G(F)(x, z) + LF(z)$$

where L is defined by (34). We then recast (35) as

$$F(Z_t^\epsilon) = F(Z_0) + \int_0^t G(F)(Y_s^\epsilon) ds + \int_0^t LF(Z_s^\epsilon) ds + M_t^\epsilon. \quad (37)$$

We are now left with passing to the limit $\epsilon \rightarrow 0$ in (37).

Consider first the second term of the right-hand side of (37). We have the following result (compare with Proposition 2.8):

Proposition 3.2. *For any bounded function F defined on \mathbb{Z} and any $t \geq 0$, under the assumptions of Theorem 3.1, we have*

$$\mathbb{E} \left[\left(\int_0^t G(F)(Y_s^\epsilon) ds \right)^2 \right] \longrightarrow 0 \quad \text{as } \epsilon \rightarrow 0,$$

where $G(F)$ is defined by (36).

Proof. The proof follows the same steps as that of Proposition 2.8. Fix $z \in \mathbb{Z}$ and consider the function $x \in M \mapsto G_z(x) = G(F)(x, z)$, that we identify with a vector in \mathbb{R}^m , denoted G_z . Using (33), we observe that $\pi^T G_z = 0$. We then deduce that, for any $y \in \mathbb{R}^m$ such that $y^T(Q - \Delta) = 0$ (where Δ has been defined in Remark 2.2), we have $y^T G_z = 0$. We then infer from Lemma 2.4 that there exists $u_z \in \mathbb{R}^m$ such that $(Q - \Delta)u_z = G_z$. Introducing the function $u(x, z) = u_z(x)$, we easily check that $\bar{L}^0 u = G(F)$. The rest of the proof is identical to that of Proposition 2.8. \square

For the other terms of (37), the proof follows exactly the same steps as in the proof of Theorem 2.3. We hence obtain that the weak limit Z of (Z^ϵ) satisfies that, for every bounded function F on \mathbb{Z} , there exists a martingale M^F such that

$$F(Z_t) = F(Z_0) + \int_0^t LF(Z_s) ds + M_t^F. \quad (38)$$

Using Lemma A.2, we conclude that Z is a jump process of generator L defined by (34).

Remark 3.3. We refer to [10] for the study of the limit process introduced in Theorem 3.1, after a rescaling both in time and space. We show there that it converges to a Brownian motion (up to a multiplicative constant).

3.2 Numerical illustration

We have simulated the model described in Section 3.1, with the choices

$$Q = \begin{pmatrix} 0 & q & & & \\ q & 0 & q & & \\ \ddots & \ddots & \ddots & & \\ & & q & 0 & q \\ & & & q & 0 \end{pmatrix},$$

$$C_l = \begin{pmatrix} 0 & \cdots & 0 & c_l \\ 0 & \cdots & 0 & \\ \vdots & & & \vdots \\ 0 & 0 & \cdots & 0 \end{pmatrix} \quad \text{and} \quad C_r = \begin{pmatrix} 0 & \cdots & 0 & 0 \\ 0 & \cdots & 0 & \\ \vdots & & & \vdots \\ c_r & 0 & \cdots & 0 \end{pmatrix}$$

with $q = 1$, $c_r = 2$, $c_l = 1$, $m = 5$ and the initial condition $Y_0 = (0, 0)$ (similar results are obtained for other initial conditions). The parameters λ_r and λ_l of the macroscopic evolution are

$$\lambda_l = \frac{c_l}{m} = \frac{1}{5} \quad \text{and} \quad \lambda_r = \frac{c_r}{m} = \frac{2}{5}.$$

We first monitor the convergence of the distribution of S_0^ϵ , the exit time from the first well. On Fig. 11, we show its empirical expectation and variance. We see that they converge to their asymptotic values as ϵ goes to zero. This convergence is confirmed by the histogram representation (on Fig. 12), where we see a good agreement between the discrete curve and the asymptotic curve for sufficiently small values of ϵ . Likewise, the L^1 error, also shown on Fig. 12, indeed converges to zero.

We next study the distribution of the amplitude of the first jump of the macroscopic variable Z^ϵ , that is the distribution of the random variable

$$\Delta Z^\epsilon := Z_{S_0^\epsilon}^\epsilon - Z_0.$$

On Fig. 13, we show the empirical expectation and variance of ΔZ^ϵ , which are observed to converge to their asymptotic values. Note that the limiting

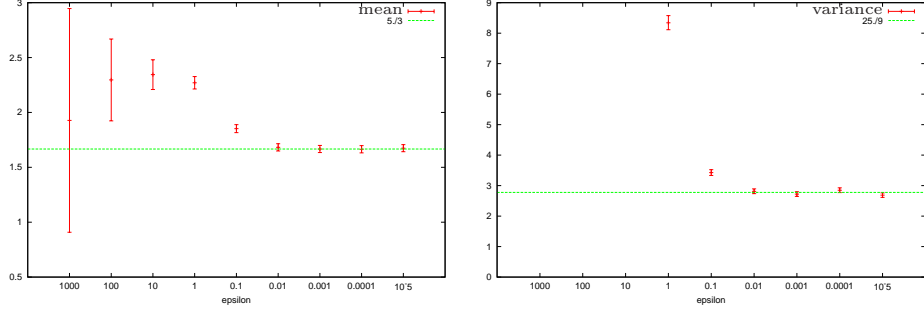


Figure 11: Empirical expectation (left) and variance (right) of S_0^ϵ as a function of ϵ .

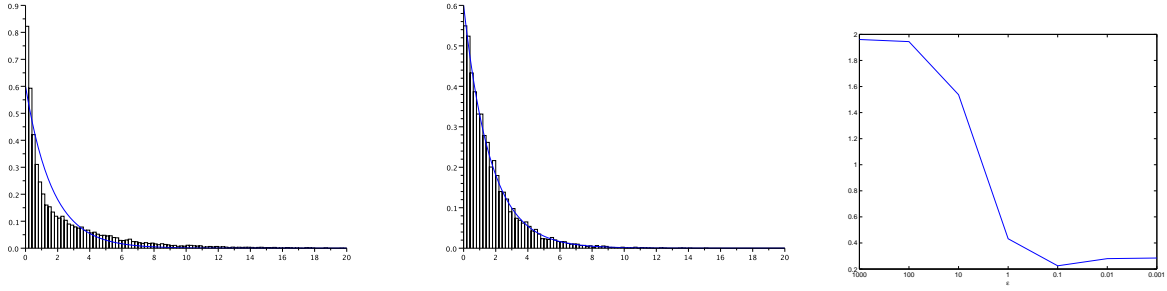


Figure 12: Left and Center: Distribution of S_0^ϵ , the first exit time from a macro-state (Left: large $\epsilon = 1$. Center: small $\epsilon = 10^{-3}$). Right: L^1 error (30) on the distribution of S_0^ϵ , as a function of ϵ .

process Z , the generator of which is the operator (34), drifts to the right, since $\lambda_r > \lambda_l$. We compute that

$$\mathbb{E}(\Delta Z) = \mathbb{P}(\Delta Z = 1) \times 1 + \mathbb{P}(\Delta Z = -1) \times (-1) = \frac{2/5}{3/5} - \frac{1/5}{3/5} = \frac{1}{3},$$

and we indeed see on Fig. 13 that $\lim_{\epsilon \rightarrow 0} \mathbb{E}(\Delta Z^\epsilon) = \mathbb{E}(\Delta Z)$. On Fig. 14, we show the empirical distribution of ΔZ^ϵ for a small ϵ , and we observe that

$$\mathbb{P}(\Delta Z^\epsilon = 1) \approx \mathbb{P}(\Delta Z = 1) = \frac{2}{3}, \quad \mathbb{P}(\Delta Z^\epsilon = -1) \approx \mathbb{P}(\Delta Z = -1) = \frac{1}{3}.$$

We also check on Fig. 14 that the L^1 error between the distribution of ΔZ^ϵ and that of ΔZ goes to 0 as ϵ goes to zero.

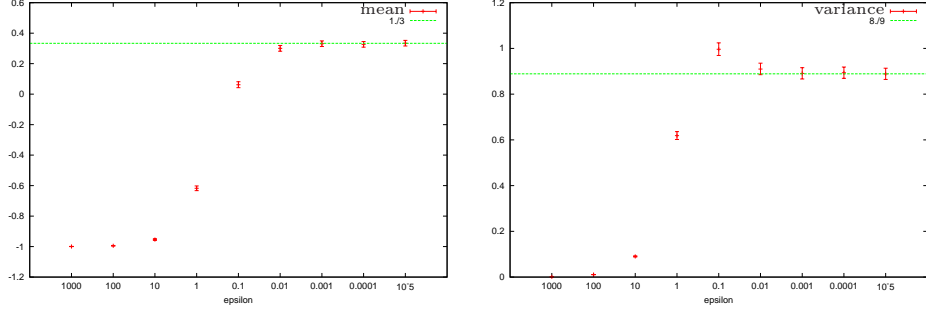


Figure 13: Empirical expectation (left) and variance (right) of ΔZ^ϵ as a function of ϵ .

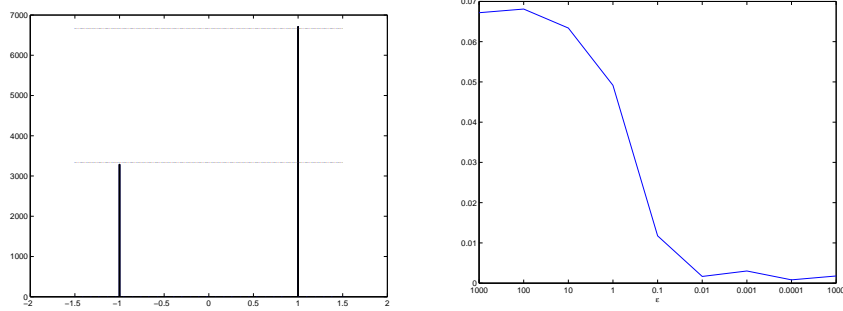


Figure 14: Left: Empirical estimation of the probabilities $\mathbb{P}(\Delta Z^\epsilon = -1)$ and $\mathbb{P}(\Delta Z^\epsilon = 1)$ for $\epsilon = 10^{-5}$. Right: L^1 error (30) on the distribution of ΔZ^ϵ as a function of ϵ .

4 Exchange of energy in a system of two particles

In this final section, we consider a more elaborate model. This model is composed of two particles. The state of the first (resp. second) particle is described by the vector X (resp. Z) with k components. An energy functional \mathcal{E} is associated to each particle. The system evolves either due to the internal evolution within a particle, or due to the interaction between the two particles. In the first case, the energy of each particle is preserved. In the second case, the internal energy of each particle varies, but the total energy of the system, $\mathcal{E}(X) + \mathcal{E}(Z)$, is preserved. Interactions between the particles occur on a much slower time scale than the internal evolution of each particle. One must hence wait for a long time before observing any

change in each particle energy.

The model is presented in details in Section 4.1. In Section 4.2, we establish a convergence result on the time evolution of the energy of the first particle, which is our macroscopic variable of interest. We only give there a sketch of the proof as it follows the same arguments as before.

One of the interesting features of this model is that the macroscopic variable of interest is *not* one cartesian coordinate of the system. We show that the arguments used in Sections 2 and 3 carry over to this more general case.

4.1 Presentation of the model

We consider a model with two particles. Each particle contains k spin-like variables, that can take the value 0 (spin down) or 1 (spin up). At time t , the state of the system is given by $\bar{Y}_t^\epsilon = (\bar{X}_t^\epsilon, \bar{Z}_t^\epsilon) \in M \times M$, where $M = \{0, 1\}^k$ is the space for the k spins of each particle. For each particle, we are given an energy functional $\mathcal{E}(x) = \mathcal{E}(x_1, \dots, x_k)$ (with $x_j \in \{0, 1\}$, $1 \leq j \leq k$) that depends on the state of the k spins of the particle. One choice is to set $\mathcal{E}(x) = x_1 + \dots + x_k$, which would correspond (up to a multiplicative factor) to the energy of k spins in a uniform magnetic field.

The intensity matrix of the process \bar{Y}^ϵ is built as follows:

- the internal dynamic of each particle is governed by an intensity matrix Q that conserves its energy, i.e. $Q(x, x') = 0$ if $\mathcal{E}(x) \neq \mathcal{E}(x')$. We define the global internal dynamic intensity matrix \bar{Q}^0 by

$$\begin{aligned}\bar{Q}^0((x, z), (x', z')) &= Q(x, x') \quad \text{if } x \neq x', \\ \bar{Q}^0((x, z), (x, z')) &= Q(z, z') \quad \text{if } z \neq z', \\ \bar{Q}^0((x, z), (x', z')) &= 0 \quad \text{if } x \neq x' \text{ and } z \neq z' .\end{aligned}$$

- the coupling between the two particles is described by a matrix C . This coupling introduces an exchange of energy between the two particles, while keeping the total energy constant. We assume that C is such that

$$C((x, z), (x', z')) = 0 \text{ if } \mathcal{E}(x) + \mathcal{E}(z) \neq \mathcal{E}(x') + \mathcal{E}(z') \text{ or if } \mathcal{E}(x) = \mathcal{E}(x').$$

- the transition intensities of the process Y^ϵ are given by

$$\bar{Q}^\epsilon = \bar{Q}^0 + \epsilon C.$$

We make the following assumption:

$$\begin{aligned}
& \text{the matrix } Q \text{ is such that, for every admissible energy level } e, \\
& \text{the state class of energy } e \text{ is irreducible} \\
& \text{and thus admits a unique invariant probability measure } \bar{\pi}^e.
\end{aligned} \tag{39}$$

We denote by π^e the probability measure on M defined by $\pi^e(x) = \bar{\pi}^e(x)$ if $\mathcal{E}(x) = e$ and $\pi^e(x) = 0$ otherwise. Any normalized linear combination of the measures π^e (with non-negative coefficients) is thus an invariant probability measure of Q . We consider the state classes of $M \times M$ such that the energy of each particle stays constant. These classes are irreducible and admit a unique invariant probability measure $\pi^e \otimes \pi^{e'}$. The invariant probability measures of \bar{Q}^0 are of the form $(Z')^{-1} \sum_{e,e'} Z(e, e') \pi^e \otimes \pi^{e'}$, where $Z(e, e') \geq 0$ are some coefficients and where Z' is a normalization constant.

4.2 Main result

As pointed out above, our quantity of interest is $\mathcal{E}(\bar{X}_t^\epsilon)$, the energy of the first particle. In view of the chosen scaling in \bar{Q}^ϵ , the characteristic time scale of evolution of this energy is of the order of ϵ^{-1} . We thus need to rescale in time the evolution, and therefore introduce $Y_t^\epsilon = (X_t^\epsilon, Z_t^\epsilon) := \bar{Y}_{t/\epsilon}^\epsilon$ and $\mathcal{E}_t^\epsilon = \mathcal{E}(\bar{X}_{t/\epsilon}^\epsilon)$.

We now identify the limit of the process \mathcal{E}_t^ϵ , and state the main convergence result of that section, namely Theorem 4.1 below. Let L^ϵ be the generator of $(Y_t^\epsilon)_{t \geq 0}$, which is a jump process of intensity matrix $Q^\epsilon = \epsilon^{-1} \bar{Q}^\epsilon$. We have

$$L^\epsilon \varphi(x, z) = \sum_{x', z' \in M} Q^\epsilon((x, z), (x', z')) [\varphi(x', z') - \varphi(x, z)].$$

For a function $\varphi(x, z) = F(x)$ that only depends on the state of the first particle, we have

$$\begin{aligned}
(L^\epsilon F)(x, z) &= \sum_{x', z' \in M} Q^\epsilon((x, z), (x', z')) [F(x') - F(x)] \\
&= \epsilon^{-1} \sum_{x' \in M} Q(x, x') [F(x') - F(x)] \\
&\quad + \sum_{x', z' \in M} C((x, z), (x', z')) [F(x') - F(x)].
\end{aligned}$$

Now choosing $F = \mathcal{E}$, we obtain

$$l(x, z) := (L^\epsilon \mathcal{E})(x, z) = \sum_{x', z' \in M} C((x, z), (x', z')) [\mathcal{E}(x') - \mathcal{E}(x)]$$

since $Q(x, x') = 0$ if $\mathcal{E}(x') \neq \mathcal{E}(x)$. We suppose that, at the initial time, the energy of each particle is independent of ϵ : $\mathcal{E}(X_0^\epsilon) = E_x$ and $\mathcal{E}(Z_0^\epsilon) = E_z$, where E_x and E_z are independent of ϵ . The total initial energy is denoted $E = E_x + E_z$.

Using Proposition A.1, we see that there exists a martingale M_t^ϵ such that

$$\mathcal{E}_t^\epsilon = E_x + \int_0^t l(X_s^\epsilon, Z_s^\epsilon) ds + M_t^\epsilon. \quad (40)$$

As in Section 2.2, we can show that there exists a process \mathcal{E} such that \mathcal{E}^ϵ converges to \mathcal{E} , up to extraction. We now identify the distribution of the process \mathcal{E} and show that it is independent of the chosen sub-sequence (thereby proving that all the sequence \mathcal{E}^ϵ converges to \mathcal{E} , and not only a subsequence).

We introduce the average of the drift in (40) with respect to an invariant measure of \overline{Q}^0 :

$$\begin{aligned} \tilde{l}(e_1, e_2) &= \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} l(x, z) \pi^{e_1}(x) \pi^{e_2}(z) \\ &= \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} \pi^{e_1}(x) \pi^{e_2}(z) \sum_{x', z' \in M} C((x, z), (x', z')) [\mathcal{E}(x') - \mathcal{E}(x)] \\ &= \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} \pi^{e_1}(x) \pi^{e_2}(z) \sum_{\substack{x', z' \text{ s.t.} \\ \mathcal{E}(x') + \mathcal{E}(z') = e_1 + e_2}} C((x, z), (x', z')) [\mathcal{E}(x') - e_1]. \end{aligned}$$

We further define

$$f(x, z) = l(x, z) - \tilde{l}(\mathcal{E}(x), \mathcal{E}(z))$$

and

$$g(e) = \tilde{l}(e, E - e), \quad (41)$$

and recast (40) as

$$\mathcal{E}_t^\epsilon = E_x + \int_0^t f(X_s^\epsilon, Z_s^\epsilon) ds + \int_0^t g(\mathcal{E}_s^\epsilon) ds + M_t^\epsilon. \quad (42)$$

We now want to pass to the limit $\epsilon \rightarrow 0$ in (42).

Consider the second term in the right-hand side of (42). By construction, f is the difference between the function l and its average \tilde{l} . The average of f is thus expected to vanish. This is indeed the case: for any two energies e_1 and e_2 , we compute

$$\begin{aligned}
(\pi^{e_1} \otimes \pi^{e_2})^T f &= \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} \pi^{e_1}(x) \pi^{e_2}(z) f(x, z) \\
&= \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} \pi^{e_1}(x) \pi^{e_2}(z) l(x, z) - \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} \pi^{e_1}(x) \pi^{e_2}(z) \tilde{l}(e_1, e_2) \\
&= \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e_1 \\ z \text{ s.t. } \mathcal{E}(z)=e_2}} \pi^{e_1}(x) \pi^{e_2}(z) l(x, z) - \tilde{l}(e_1, e_2) \\
&= 0.
\end{aligned}$$

Therefore, for any μ such that $\mu^T \bar{L}^0 = 0$, we have $\mu^T f = 0$. Following the arguments of Proposition 2.8, we deduce that, for any t , the random variable $\int_0^t f(X_s^\epsilon, Z_s^\epsilon) ds$ converges to 0 in $L^2(\Omega)$, and that the random process also weakly converges to 0.

We now turn to the third term of the right-hand side of (42), and claim that (up to the extraction of a sub-sequence)

$$\int_0^t g(\mathcal{E}_s^\epsilon) ds \Rightarrow \int_0^t g(\mathcal{E}_s) ds, \quad (43)$$

where \mathcal{E}_s is such that $\mathcal{E}_s^\epsilon \Rightarrow \mathcal{E}_s$. The function g is defined on the set $\mathcal{E}(M)$ of the admissible energies, which is a finite set (we recall that $M = \{0, 1\}^k$). We denote by \tilde{g} the P1 interpolation of g on \mathbb{R} , which is a piecewise linear function defined on \mathbb{R} and that coincides with g on $\mathcal{E}(M)$. The function \tilde{g} being Lipschitz on \mathbb{R} , we infer from Lemma 2.6 that the function $\Phi : x \mapsto \left(\int_0^t \tilde{g}(x_s) ds \right)_t$ is continuous. Therefore, the convergence $\mathcal{E}_s^\epsilon \Rightarrow \mathcal{E}_s$ implies that

$$\left(\int_0^t g(\mathcal{E}_s^\epsilon) \right) = \left(\int_0^t \tilde{g}(\mathcal{E}_s^\epsilon) \right) \text{ converges to } \left(\int_0^t \tilde{g}(\mathcal{E}_s) \right) = \left(\int_0^t g(\mathcal{E}_s) \right).$$

We thus have proved (43).

We next turn to the last term in the right-hand side of (42). As in the previous sections, we can show that M^ϵ weakly converges (up to extraction) to some martingale M .

We can now pass to the limit $\epsilon \rightarrow 0$ in (42), and obtain that the limit process \mathcal{E} satisfies

$$\mathcal{E}_t = E_x + \int_0^t g(\mathcal{E}_s) ds + M_t. \quad (44)$$

It is now easy to recast the above equation in a more useful form. In view of (41), we indeed note that

$$g(e) = \underbrace{\sum_{e'} \sum_{\substack{x \text{ s.t. } \mathcal{E}(x)=e \\ z \text{ s.t. } \mathcal{E}(z)=E-e}} \sum_{\substack{x' \text{ s.t. } \mathcal{E}(x')=e' \\ z' \text{ s.t. } \mathcal{E}(z')=E-e'}} \pi^e(x) \pi^{E-e}(z) C((x, z), (x', z')) (e' - e)}_{B_E(e, e')}.$$

Therefore, the equation (44) reads

$$\mathcal{E}_t = E_x + \int_0^t \sum_{e'} B_E(\mathcal{E}_s, e') (e' - \mathcal{E}_s) ds + M_t,$$

where, we recall, E is the total energy of the system, which is preserved along the dynamics.

We conclude this formal approach by pointing out that the above equation actually does not allow to identify the law of the process $(\mathcal{E}_t)_t$. In the proof of Theorem 2.3 (see Section 2.2), we performed that step of the proof by using Lemma 2.5, which is not possible in our context here. To identify the law of the process $(\mathcal{E}_t)_t$, we resort to Lemma A.2. Consider a bounded function φ on $\mathcal{E}(M)$, and the martingale

$$M_t^{\varphi, \epsilon} := \varphi(\mathcal{E}_t^\epsilon) - \varphi(E_x) - \int_0^t \sum_{e'} B_E(\mathcal{E}_s^\epsilon, e') (\varphi(e') - \varphi(\mathcal{E}_s^\epsilon)) ds.$$

Following the same steps as above, we show that each term converges when ϵ goes to zero. In particular, $M_t^{\varphi, \epsilon}$ converges to a martingale M^φ that satisfies

$$M_t^\varphi = \varphi(\mathcal{E}_t) - \varphi(E_x) - \int_0^t \sum_{e'} B_E(\mathcal{E}_s, e') (\varphi(e') - \varphi(\mathcal{E}_s)) ds.$$

Lemma A.2 then implies that \mathcal{E} is a jump process of intensity matrix $B = B_E(e, e')$.

We thus have the following result:

Theorem 4.1. *We denote by \mathcal{P}^ϵ the distribution of the process (\mathcal{E}^ϵ) , where we assumed that the initial condition (E_x, E_z) is independent of ϵ . We denote by \mathcal{P} the distribution of the jump process of initial condition E_x and of intensity matrix $B = B_E(e, e')$, with $E = E_x + E_z$. Under the assumptions on the matrices Q and C described in Section 4.1, we have*

$$\mathcal{P}^\epsilon \Rightarrow \mathcal{P} \text{ as } \epsilon \rightarrow 0.$$

4.3 Numerical illustration

We have numerically simulated the system described above, when each particle has two spins, i.e. $k = 2$. In this case, $\text{Card}(M) = 4$, and the admissible states for each particle are labelled as 1: $\downarrow\downarrow$, 2: $\uparrow\downarrow$, 3: $\downarrow\uparrow$ and 4: $\uparrow\uparrow$. The energy of each particle is the sum of the energies of its two spins, which are equal to 0 (spin down, \downarrow) or 1 (spin up, \uparrow). The matrix Q that governs the internal dynamic of each particle is of the form

$$Q = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & -q_1 & q_1 & 0 \\ 0 & q_2 & -q_2 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

This matrix preserves the energy of the particle as it only allows transitions between states of the same energy (namely, $\uparrow\downarrow$ and $\downarrow\uparrow$). We work with $q_1 = 10$ and $q_2 = 1$.

There are five possible initial energies for the complete system:

- $E = 0$ (both particles are initially in the state 1: $\downarrow\downarrow$). The system then does not evolve, as only one state corresponds to that total energy. The case when $E = 4$ is similar.
- $E = 1$: initially, one particle is in the state 1: $\downarrow\downarrow$, while the other particle is in the state 2: $\uparrow\downarrow$ or 3: $\downarrow\uparrow$. We consider this case below. Note that the case when $E = 3$ is similar.
- $E = 2$: without loss of generality, we may assume that the initial state of each particle is 2: $\uparrow\downarrow$.

In what follows, we only consider the case $E = 1$. We have checked that results obtained in the case $E = 2$ lead to the same qualitative conclusions.

As mentioned above, we assume that the initial state of the first particle is 2: $\uparrow\downarrow$ (corresponding to the energy $E_x = 1$), and that the initial state of the second particle is 1: $\downarrow\downarrow$ (corresponding to the energy $E_z = 0$).

The matrix C (which encodes how the two particles interact) is chosen of the form

$$\begin{aligned} C((2, z), (x', z')) &= c_1 \text{ if } \mathcal{E}(x) + \mathcal{E}(z) = \mathcal{E}(x') + \mathcal{E}(z') \text{ and } \mathcal{E}(x) \neq \mathcal{E}(x'), \\ C((x, z), (x', z')) &= c_2 \text{ if } x \neq 2 \text{ and } \mathcal{E}(x) + \mathcal{E}(z) = \mathcal{E}(x') + \mathcal{E}(z') \text{ and } \mathcal{E}(x) \neq \mathcal{E}(x'), \\ C((x, z), (x', z')) &= 0 \text{ otherwise.} \end{aligned}$$

We work with $c_1 = 1$ and $c_2 = 0.2$.

We monitor the distribution of S_0^ϵ , the first waiting time before an exchange of energy between the two particles occurs. Figures 15 and 16 show the convergence of the distribution of S_0^ϵ to the asymptotic distribution, which is an exponential distribution of parameter $B(1, 0) = 6/11$.

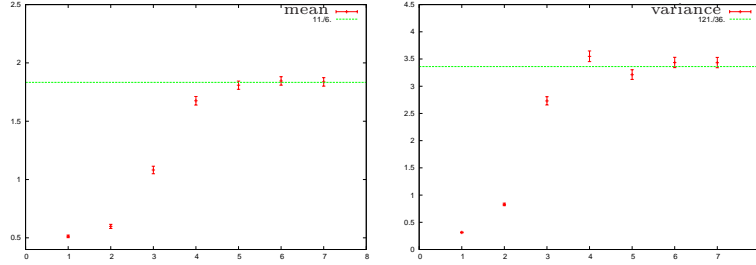


Figure 15: Empirical expectation (left) and variance (right) of S_0^ϵ as a function of ϵ .

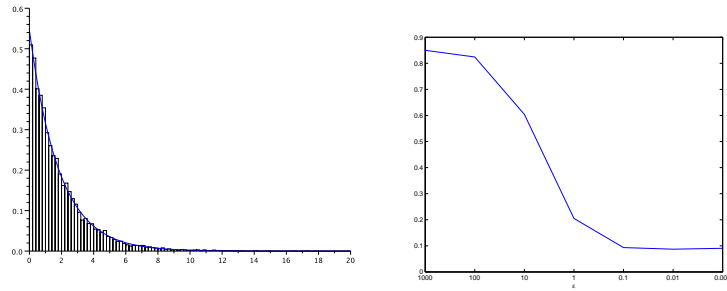


Figure 16: Left: Distribution of the first waiting time S_0^ϵ before the energy of the first particle changes ($\epsilon = 10^{-3}$); Right: L^1 error (30) between the distribution of S_0^ϵ and its limit distribution.

Acknowledgments

The models we consider here and the questions we study were suggested to us by Stefano Olla. We thank him for his suggestions and the fruitful discussions we had with him. We also thank Eric Cancès for his constant support throughout this research project. We thank Tony Lelièvre for his careful reading of a previous version of this article. The research leading to these results has received funding from the European Research Council under the European Community's Seventh Framework Programme (FP7/2007-2013 Grant Agreement MNIQS no. 258023).

A Some useful results

For convenience, we recall in this Appendix some classical results of probability theory that are needed in this article.

Martingales Several results on martingales are useful in this work. The first one is an existence and uniqueness result for the martingale problem introduced by D.W. Stroock and S.R.S. Varadhan (see e.g. [1] and [19]):

Proposition A.1 (Lemma 5.1 of Appendix 1 of [9]). *Let $(X_t)_{t \geq 0}$ be a Markov process and let $(\mathcal{F}_t)_{t \geq 0}$ be its natural filtration. For any bounded function F , we introduce*

$$M_t^F = F(X_t) - F(X_0) - \int_0^t L F(X_s) ds$$

and

$$N_t^F = (M_t^F)^2 - \int_0^t (L F^2(X_s) - 2F(X_s) L F(X_s)) ds,$$

where L is the generator of the Markov process (X_t) . Then M^F and N^F are \mathcal{F}_t -martingales. In particular, the quadratic variation of M^F reads

$$\langle M^F \rangle_t = \int_0^t (L F^2(X_s) - 2F(X_s) L F(X_s)) ds.$$

We recall that for a continuous local martingale M , the process $\langle M \rangle$ is defined to be the unique right-continuous and increasing predictable process starting at zero such that $M^2 - \langle M \rangle$ is a local martingale.

The next result is of paramount importance to prove that a process is a jump process, and to identify its generator. We state here this result as a simplified version of [8, Theorem 21.11].

Lemma A.2 (Uniqueness result for the martingale problem). *Let F be a countable space, Z_t a stochastic process valued in F and L an operator on bounded functions $\varphi : F \rightarrow \mathbb{R}$ defined by*

$$L\varphi(x) = \sum_{x' \in F} L_{x,x'} (\varphi(x') - \varphi(x)),$$

where $L_{x,x'} \geq 0$ for any $x, x' \in F$ and $\sup_{x,x' \in F} L_{x,x'} < \infty$. If for any bounded function $\varphi : F \rightarrow \mathbb{R}$, the process

$$M_t^\varphi := \varphi(Z_t) - \varphi(Z_0) - \int_0^t L\varphi(Z_s) ds$$

is a martingale w.r.t. the natural filtration of $(Z_t)_{t \geq 0}$, then $(Z_t)_{t \geq 0}$ is the jump process of initial condition Z_0 and of generator L .

Convergence of probability measures We now turn to classical results concerning the convergence of probability measures in $D_{\mathbb{R}}[0, \infty)$, which is the space of functions that are right continuous with left limits (the so-called càd-làg functions), defined on $[0, \infty)$ and valued in \mathbb{R} . Proposition A.3 gives an equivalent definition of the Skorohod metric on $D_{\mathbb{R}}[0, \infty)$ (see [4, p. 116-118] for the original definition of the Skorohod metric, that we actually do not use in this work). Theorem A.4 states convergence criteria for probability measures on $D_{\mathbb{R}}[0, \infty)$.

Proposition A.3 (Proposition 5.3, Chap. 3 of [4]). *Let $(x_n)_{n \geq 0}$ be a sequence in $D_{\mathbb{R}}[0, \infty)$ and $x \in D_{\mathbb{R}}[0, \infty)$. The following assertions are equivalent:*

- $\lim_{n \rightarrow \infty} x_n = x$ in the space $D_{\mathbb{R}}[0, \infty)$ endowed with the Skorohod metric.
- For any $T > 0$, there exists a sequence of strictly increasing, continuous maps $(\lambda_n)_{n \geq 0}$ defined on $[0, \infty)$ and valued in $[0, \infty)$ such that

$$\lim_{n \rightarrow \infty} \sup_{0 \leq t \leq T} |\lambda_n(t) - t| = 0 \quad (45)$$

and

$$\lim_{n \rightarrow \infty} \sup_{0 \leq t \leq T} |x_n(t) - x(\lambda_n(t))| = 0. \quad (46)$$

Theorem A.4 (Aldous' criterion, Theorem VI.4.5 of [7]). *Let $(X^n)_{n \geq 1}$ be a sequence of càd-làg processes, with distributions \mathcal{P}^n . Suppose that*

- for any $N \in \mathbb{N}$ and $\epsilon > 0$, there exists $n_0 \in \mathbb{N}$, $n_0 > 0$, and $K \in \mathbb{R}^+$ such that, for any $n \geq n_0$,

$$\mathcal{P}^n \left(\sup_{t \leq N} |X_t^n| > K \right) \leq \epsilon. \quad (47)$$

- for any $N \in \mathbb{N}$ and $\alpha > 0$, we have

$$\lim_{\theta \rightarrow 0} \limsup_n \sup_{S, T \in \mathfrak{T}_N^n, S \leq T \leq S + \theta} \mathcal{P}^n (|X_T^n - X_S^n| \geq \alpha) = 0, \quad (48)$$

where \mathfrak{T}_N^n is the set of all \mathcal{F}^n stopping times that are bounded by N .

Then the sequence $(X^n)_{n \in \mathbb{N}}$ is tight.

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